MEMOIRS OF THE FACULTY OF ENGINEERING
FUKUI UNIVERSITY
VOL.28 No.1 1980

Spectrophotometric Determination of Cadmium after Separation by Adsorption of Its Oxinate on Microcrystalline Naphthalene

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(Received Jan. 31, 1980)

A procedure is presented for the spectrophotometric determination of cadmium after separation by adsorption of cadmium oxinate on microcrystalline naphthalene. A water-insoluble oxinate formed with cadmium is quantitatively adsorbed from aqueous solution with microcrystalline naphthalene. This oxinate has an absorption maximum at 395 nm. The optimum pH range for the adsorption is 5.8-9.2. The molar absorptivity is 4.5×10^3 $l \cdot mol^{-1} \cdot cm^{-1}$ at 395 nm, the sensitivity being 2.5×10^{-2} μg of cadmium per cm^{-2} for an absorbance of 0.001. Ten samples containing 100 μg of cadmium gave a mean absorbance of 0.403 with a relative standard deviation of 2.8%. Effect of optimum wavelength, amounts of reagent and naphthalene, digestion time, standing time, shaking time and diverse ions are studied.

1. Introduction

Oxine(8-hydroxyquinoline) reacts with various metal ions to form very stable water-insoluble colored oxinates which are easily extracted into ordinary organic solvents such as chloroform or benzene, and the trace amounts of metals have been determined spectrophotometry. However, this method cannot be applied for zinc, magnesium and cadmium, because their oxinates are mostly insoluble in ordinary organic solvents mentioned above, owing to their strongly hydrated structure. If the hydrated water molecules in the chelate are replaced by other neutral organic molecules, the chelate can be extracted into nonreactive organic solvents. For example, magnesium oxinate is extracted into chloroform in the presence of pyridine[1], n-butylamine[2] and butylcello-

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solve[3), 4)], while zinc oxinate is extracted when pyridine[5)] is added. Cadmium oxinate is not extracted by such a method because it is hydrated more strongly than zinc and magnesium oxinates.

We have already reported on the spectrophotometric determination of cadmium after molten naphthalene extraction of its oxinate[6)]. This method is based on the formation of the cadmium oxinate and its extraction into molten naphthalene. After drying of the naphthalene mixture, it is dissolved in dimethylformamide and cadmium analysed spectrophotometrically.

Recently we have developed a new method involving solid-liquid separation after adsorption of the chelate on microcrystalline naphthalene, whereby the trace amounts of metals are determined spectrophotometrically[7), 8), 9)]. In the present paper, cadmium was chosen as a metal to be determined, and its oxinate was adsorbed completelyon microcrystalline naphthalene from aqueous solution at pH 5.8-9.2. The adsorbed naphthalene crystals containing the cadmium oxinate were separated and dissolved in dimethylformamide, and the absorbance of the solution was measured at 395 nm. The method appears promising since the adsorption of the cadmium oxinate on naphthalene is rapid and can be carried out by vigorous shaking for about 1 min at room temperature compared with the molten naphthalene extraction method at high temperature[6)] that requires a much longer operation period. It was applied for the spectrophotometric determination of trace amounts of various metals.

2 Experimental method

2.1 Reagents

Standard cadmium solution, 10 ppm : Prepared by diluting 10 ml of 1000-ppm standard cadmium solution (Wako Pure Chemical co. Osaka, Japan) to 1000 ml with water.

Oxine solution, 1% : Prepared by dissolving 1 g of oxine in 2 ml of glacial acetic acid on a water bath, and diluting to 100 ml with water

Naphthalene acetone solution, 20% : Prepared by dissolving 20 g of naphthalene in acetone and diluting to 100 ml.

Buffer solutions were prepared by mixing 1M acetic acid and 1M ammonium acetate solution for pH 3-6, or 1M aqueous ammonia and 1M ammonium acetate solution for pH 8-11.

Naphthalene, acetone, dimethylformamide and all other reagents were of analytical-reagent grade, and were used without further purification.

Water was purified by passage through a demineralizer.

2.2 Apparatus

A Hitachi Model 200-20 double beam spectrophotometer with 10 mm glass cells was used for the absorbance measurements.

All pH measurements were done with a Toa-Dempa pH meter, equipped with combined calomel and glass electrodes.

The naphthalene was dried with a Tabai Model K-2 dryer(Tabai Mfg. Co. Ltd., Japan).

2.3 Procedure

To about 45 ml of sample solution containing 20 - 260 μg of cadmium in a 100-ml tightly stoppered Erlenmeyer flask, add 1.5 ml of 1% oxine solution and adjust to pH 9.0 with 2.0 ml of the buffer. Mix the solution well, let stand for 20 min in hot water(40-50 °C) to precipitate cadmium oxinate completely. Then add 2.5 ml of 20% naphthalene solution and shake vigorously for 1.5 min. Filter off on a filter paper(e.g., No.5C, Toyo Roshi Co., Japan) placed flat on a filter plate in a funnel, or glass filter(No.2 or 3). Wash with water and dry at 50-60 °C. Dissolve the solid in dimethylformamide, make up to 10 ml, and measure the absorbance in a 10-mm glass cell at 395 nm against a reagent blank prepared similarly.

3 Results and discussion

3.1 Absorption spectra

The absorption spectra of oxine and cadmium oxinate in naphthalene dimethylformamide solution, measured against water, are shown in Fig.1. The cadmium oxinate has one absorption maximum at 395 nm. The reagent blank shows strong absorption below 370 nm. There is practically negligible absorption due to the reagent blank at 395 nm peak of absorption for cadmium oxinate. Therefore, all the absorbance measurements were performed at 395 nm.

Effect of pH

The effect of pH on the recovery of the cadmium oxinate is shown in Fig.2. The pH measurements on the aqueous solution after adsorption were made at room temperature. The pH region of 5.8-9.2 seems suitable for quantitative recovery.

Effect of reagent concentration and buffer solution

Various amounts of oxine were added to the solutions containing 100 μg of cadmium at pH about 9.0, and the effect of variation in the

oxine concentration on the absorbance was studied. The results are shown in Fig.3. The absorbance increases with increasing amounts of oxine up to 0.1 ml of 1% oxine solution, whereafter addition of 0.1-2.5 ml had always maximum absorbance, with slight increase in the absorbance when more than 2,5 ml was added. Thus, 1.5 ml of oxine solution were used for all further studies. Varying the volume of the buffer solutions from 0.5 to 4.0 ml at pH 9.0 did not affect the absorbance.

Effect of digestion time and naphthalene concentration

The cadmium oxinate containing 100 μg of cadmium was warmed in a hot water bath at 40-50 °C and the effect of digestion time on the absorbance was investigated between 10 and 30 min. No variation in the

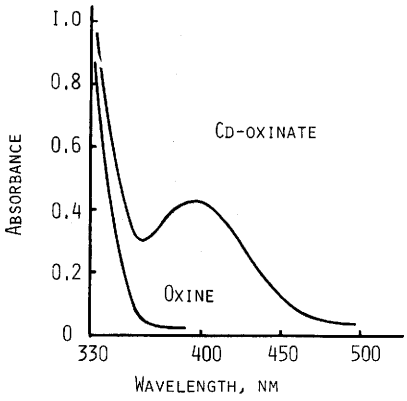

Fig. 1 Absorption spectra of oxine and cadmium oxinate in naphthalene-DMF solution
Cd : 100 μg ; pH : 9.0 ; 1% oxine : 1.5 ml ; Digestion time : 20 min ; 20% naphthalene : 2.5 ml ; Shaking time : 1.5 min
Reference : Water

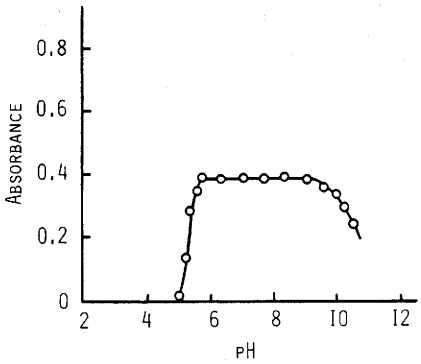

Fig. 2 Effect of pH
Cd : 100 μg ; Wavelength : 395 nm ; 1% oxine : 1.5 ml ; Digestion time : 20 min ; 20% naphthalene : 2.5 ml ; Shaking time : 1.5 min
Reference : Reagent blank

absorbance was seen for this period of digestion. In this experiments, 20 min digestion period was selected for convenience. Varying amounts of naphthalene were added to the solution containing the cadmium oxinate, and the adsorption was carried out by the described procedure. The results are shown in Fig.4. The absorbance increases with increasing amounts of naphthalene up to 1.1 ml of 20% naphthalene acetone solution, and when more than 1.1 ml of it was added, the absorbance became almost constant. Therefore, 2.5 ml of 20% naphthalene solution were added for the absorbance measurements.

Effect of shaking time

The effect of shaking time on the absorbance of the cadmium oxinate was also investigated. The experimental results show that the absorbance increased with increasing shaking time up to 40 seconds, and became almost constant in the region of 40-180 seconds. Therefore, shaking time for 90 seconds was found enough for complete adsorption.

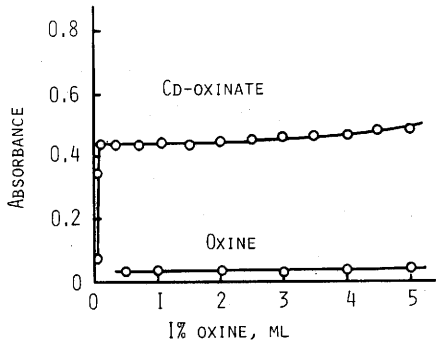

FIG. 3 EFFECT OF REAGENT CONCENTRATION
Cd : 100 μg ; pH : 9.0 ; DIGESTION TIME : 20 MIN ; 20% NAPHTHALENE : 2.5 ML
REFERENCE : REAGENT BLANK

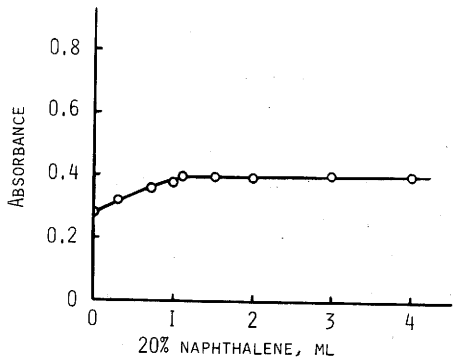

FIG. 4 EFFECT OF NAPHTHALENE CONCENTRATION
Cd : 100 μg ; WAVELENGTH : 395 NM ; pH : 9.0 ; 1% OXINE : 1.5 ML ; SHAKING TIME : 1.5 MIN
REFERENCE : REAGENT BLANK

Effect of aqueous volume

The volume of aqueous phase was varied between 50 and 400 ml while other factors were kept constant. Figure 5 shows the effect of aqueous volume on the absorbance. The absorbance was almost constant up to about 200 ml, but decreased gradually with increase in volume of aqueous phase in the region of 200-400 ml. For larger volumes of aqueous phase, the adsorption was carried out by shaking for a long time while digestion at 40-50°C.

Effect of standing time

The mixture of the cadmium oxinate and naphthalene was dissolved in dimethylformamide, and the effect of standing time on the absorbance was studied. From the experimental results, it is seen that the absorbance of the cadmium oxinate is decreased by 2 and 6% after standing for 1 to 2 hours, respectively. Thus standing for 15 min was selected for the absorbance measurements.

Calibration curve

With the optimum conditions described above, the absorbances of various concentrations of cadmium were measured at 395 nm against the

reagent blank. The calibration curve showed linearity over the range 1.2-25.6 μg of cadmium in 10 ml of dimethylformamide. The molar absorptivity was calculated to be $4.5 \times 10^3 l \cdot mol^{-1} \cdot cm^{-1}$ at 395 nm, the sensitivity being 2.48×10^{-2} μg of cadmium per cm^{-2} for an absorbance of 0.001. Ten determinations of the sample solutions containing 100 μg of cadmium gave a mean absorbance of 0.403 with a relative standard deviation of 2.8%.

Choice of solvent

The tests were made with various organic solvents to dissolve the mixture of the cadmium oxinate and naphthalene. The cadmium oxinate is soluble in dimethylformamide and dimethyl sulfoxide, but insoluble in benzene, toluene, xylene, chlorobenzene, o-dichlorobenzene, acetone, chloroform, dichloroethane, nitrobenzene and MIBK. It underwent decolorization in dioxane and acetonitrile. The solvent dimethylformamide appears appropriate for this work.

Effect of diverse ions

The effects of the diverse ions were examined with the solutions containing 100 μg of cadmium and various amounts of diverse ions(alkali metal salts or metal ions). The pH of the solution was adjusted to 9.0. The results are shown in Tables 1 and 2. The following alkali metal salts did not interfered : Na_2SO_4, NaCl, $NaH_2PO_4 \cdot 2H_2O$, $NaNO_3$, $Na_2HPO_4 \cdot 12H_2O$, CH_3COONH_4, sodium tartrate and sodium citrate. KCN and Na_2CO_3 gave positive interferences, while even small amounts of EDTA caused serious interference. Many metal ions reacting with oxine to form metal oxinates at pH 9.0 interfered with cadmium determination. Of the metal oxinates examined, Fe(III), Co(II), Ni(II), Bi(III), Cu(II), Mg(II) and Zn(II) gave positive interferences, while Pt(VI) and Cr(IV) offered negative interferences.

Table 1 Effect of diverse alkali metal salts

Alkali metal salts	Amount added(mg)	Absorbance
———	———	0.403
Na_2SO_4	200	0.407
NaCl	300	0.395
$NaH_2PO_4 \cdot 2H_2O$	100	0.389
"	300	0.385
$Na_2HPO_4 \cdot 12H_2O$	300	0.397

Na_2CO_3	100	0.429
"	300	0.433
$NaNO_3$	100	0.409
"	300	0.418
CH_3COONH_4	100	0.406
"	200	0.412
Sodium tartrate	100	0.411
"	200	0.421
Sodium citrate	300	0.414
"	500	0.407
KCN	100	0.249
EDTA	1	0.003

Cd : 100 μg ; pH : 9.0 ; 1% oxine : 1.5 ml

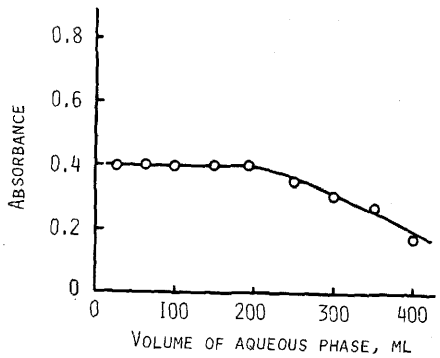

FIG. 5 EFFECT OF VOLUME OF AQUEOUS PHASE
CD : 100 UG ; WAVELENGTH : 395 NM ; PH : 9.0 ;
DIGESTION TIME : 20 MIN ; 20% NAPHTHALENE :
2.5 ML ;SHAKING TIME : 15 MIN
REFERENCE : REAGENT BLANK

Table 2 Effect of diverse metal ions

Metal ions	Amount added (μg)	Absorbance
———	———	0.403
Fe(III)	10	0.479
"	50	0.694
Co(II)	10	0.508
"	50	0.864
Ni(II)	10	0.488
"	50	0.808

Bi(III)	10	0.445
"	50	0.562
"	100	0.692
Cu(II)	10	0.525
"	50	0.837
Mg(II)	10	0.421
"	50	0.539
"	100	0.710
Pt(lV)	10	0.362
"	50	0.323
Cr(lV)	10	0.418
"	50	0.380
"	100	0.368
Zn(II)	10	0.464
"	50	0.744

Cd(II) : 100 μg ; pH : 9.0 ; 1% oxine : 1.5 ml

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